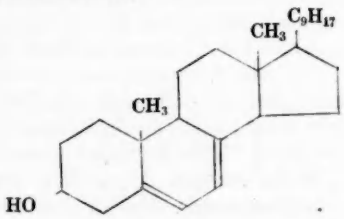
The Photochemical Dehydrogenation of Ergosterol and 7-Dehydrocholesterol.

By Toshio ANDO.

(Received March 31, 1939.)

Ergosterol undergoes dehydrogenation when its alcoholic solution containing eosin is exposed to light in the absence of oxygen.[1] The product, $C_{56}H_{86}O_2$, has been unappropriately called ergopinacone. It suffers a characteristic decomposition on submitting it to distillation in vacuum or on heating it with glacial acetic acid or decalin.[2] In this decomposition methane is eliminated, and neoergosterol is formed along with iso-dehydroergosterol, $C_{28}H_{42}O$, which has been isolated and characterized by the present author.[3]



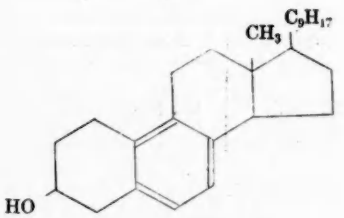
Ergosterol

↓

Ergopinacone

$C_{56}H_{86}O_2$

↓

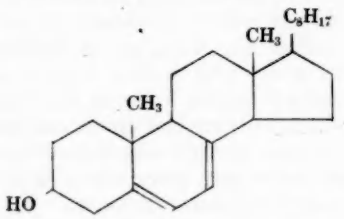


Neoergosterol

+

Iso-dehydroergosterol

$C_{28}H_{42}O$



7-Dehydrocholesterol

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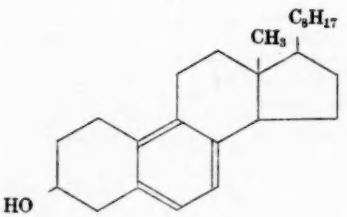
7-Dehydrocholesterol-pinacone

$C_{54}H_{86}O_2$

↓



10-Desmethyl-cholestatrienol-(3)

(Norsterol)

The analogous photochemical dehydrogenation of 7-dehydrocholesterol, with a structure similar to that of ergosterol, to 7-dehydrocholesterol-pinacone, and the decomposition of the latter to 10-desmethyl-cholesta-

(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.

(2) H. H. Inhoffen, *Ann.*, **497** (1932), 130.

(3) Y. Urushibara and T. Ando, this Bulletin **11** (1936), 757; T. Ando, *ibid.*, **13** (1938), 371; **14** (1939), 169.

trienol-(3) (norsterol) corresponding to neoergosterol have been reported independently by Urushibara and the present author[4] and by Schenck, Buchholz, and Wiese.[5] 7-Dehydrocholesterol-pinacone obtained by the present author had a lower melting point (m.p. of anhydrous substance 185.5–186°, corr.) and less water of crystallization ($C_{54}H_{86}O_2+H_2O$) than the substance described by the German authors ($C_{54}H_{86}O_2+1\frac{1}{2}H_2O$, m.p. 196–197°). The pyrolytic decomposition of 7-dehydrocholesterol-pinacone, however, yielded 10-desmethyl-cholestatrienol-(3) apparently identical with norsterol obtained by the German authors by boiling their 7-dehydrocholesterol-pinacone with acetic anhydride. Hence, it seemed possible that 7-dehydrocholesterol-pinacone exists either in two forms differing in the water of crystallization or in two isomerides differing in the configuration or in the positions of the double bonds, the differences having no influence on the constitution of the decomposition product. Ergopinacone has been often prepared in this laboratory, but the known form only has always been obtained.

In the preparation of 7-dehydrocholesterol-pinacone, the author dissolved 7-dehydrocholesterol and eosin in alcohol containing a little benzene and boiled the solution to remove air, while the German authors used alcohol solely and passed carbon dioxide. It was first assumed that such differences might have caused the production of different substances. Now the author has dehydrogenated not only 7-dehydrocholesterol but also ergosterol by these two different methods. The solutions prepared in the two ways were exposed to sunlight for several days. The specimens of the pinacones as well as their diacetates and dibenzoates which have been obtained in the two series of experiments are compared in the accompanying tables.

Table 1. Ergopinacone and Esters.

(A) The boiling method.

Substance	m.p. (corr.)	$[\alpha]_D$	Absorption maxim.
Ergopinacone[6]	200–201°		
Diacetate[6]	207–207.5°	−209° (12°)	267–268 mμ (not sharp)
Dibenzoate	206.5–207.5°	−160° (22°)	

(B) The carbon dioxide method.

Substance	m.p. (corr.)	$[\alpha]_D$	Absorption maxim.
Ergopinacone	200–201°		
Diacetate	206.5–207°	−202° (16°)	267–275 mμ (not sharp)
Dibenzoate	206.5–207.5°	−160° (16°)	280, 273 mμ[7]

(4) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802; **12** (1937), 495.

(5) F. Schenck, K. Buchholz, and O. Wiese, *Ber.*, **69** (1936), 2696.

(6) T. Ando, this Bulletin, **13** (1938), 373. The melting point of the diacetate was given formerly as 205.5–206° (corr.), but it became a little higher on further recrystallization.

(7) The sharp absorptions of the dibenzoates are undoubtedly due to the benzoyl groups.

Table 2. 7-Dehydrocholestrol-pinacone and Esters.

(A) The boiling method.

Substance	m.p. (corr.)	$[\alpha]_D$	Absorption maxim.
7-Dehydrocholesterol-pinacone	184.5-185.5°	−175° (24°) −171° (18°)[10]	
Diacetate[8]	190-190.5°	−149° (26°)	254 mμ (indistinct)
Dibenzoate[9][10]	183-183.5°	−114° (17°)	

(B) The carbon dioxide method.

Substance	m.p. (corr.)	$[\alpha]_D$	Absorption maxim.
7-Dehydrocholesterol-pinacone	184.5-185.5°	−159° (24°)	
Diacetate[8]	191-191.5°	−146° (26°)	254 mμ (indistinct)
Dibenzoate	182.5-183.5°	−113.5° (26°)	
,, [9]	182.5-183.5°	−101° (25°)	280, 273 mμ[7]

There is no doubt that the substances in the two series A and B are identical each with each. In all cases the identities were confirmed by mixed melting points. 7-Dehydrocholesterol-pinacone showed the lower melting point irrespective of the methods of removing air from the solutions of 7-dehydrocholesterol and eosin.

The pinacones and their esters all showed the colour reactions of Liebermann-Burchard and of Rosenheim as shown in the experimental part.

Another difference in the methods of preparation of 7-dehydrocholesterol-pinacone may be found in the time of exposure to sunlight. The author exposed the solutions for several days, while the German authors for a few hours. Then it is possible that the higher melting product may be formed in short exposure but changeable to the lower melting form during a longer action of sunlight. A preliminary experiment has given an indication to the possibility that it is the case. Ten hours' exposure gave a product melting at 192.5-193.5° (corr.) with decomposition after repeated recrystallization and the melting point was lowered to 187-187.5° (corr.) in a month and to 185.5-186.5° (corr.) in a year, when the substance was reserved in vacuum. Further experiments are required to decide the matter conclusively.

Experimental.

Ergopinacone and Esters.

Dibenzoate from Ergopinacone Prepared by the Boiling Method. Benzoyl chloride (5 g.) was added slowly to a solution of ergopinacone (205 mg.) in pyridine (40 c.c.) with

(8) The diacetate of the German authors showed m.p. 201 202° and $[\alpha]_D^{22°}$ -161.2°.

(9) Prepared from 7-dehydrocholesteryl benzoate. All the other esters described in the tables were prepared from the pinacones.

(10) Y. Urushibara and T. Ando, this Bulletin, **12** (1937), 495.

cooling and occasional shaking. The mixture was left to stand at room temperature overnight, and poured into ice water. The separating red matter, which solidified completely in a few days, was collected, washed with dilute acetic acid and with water, recrystallized three times from benzene-95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless, extremely fine needles (167 mg.), m.p. 201.5-202.5° (uncorr.) or 206.5-207.5° (corr.) with decomposition (Found: C, 84.92; H, 9,82. Calculated for $C_{70}H_{94}O_4$: C, 84,12; H, 9.49%). A considerable depression of the melting point was observed when the substance was mixed with the diacetate with the same melting point, but no depression with the specimen of the dibenzoate described below. $[\alpha]_D^{22°} = -160°$ (13.95 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{22°} = -2.23°$).

Preparation of Ergopinacone by the Carbon Dioxide Method. Carbon dioxide was passed through a solution of ergosterol (1 g.) and eosin (1 g.) in 95% alcohol (about 400 c.c.) for 20 minutes to remove air, and the solution was exposed to sunlight for four days. The separating needles were collected after further a week's standing, washed, and recrystallized twice from benzene-95% alcohol. Colourless silky needles (315 mg.), m.p. 200-201° (corr.) with decomposition. The substance showed the same colour reactions as the specimen prepared by the boiling method.

Diacetate. The above ergopinacone (150 mg.) was acetylated with acetic anhydride and pyridine, and the product was recrystallized twice from benzene-95% alcohol, colourless fine needles (139 mg.), m.p. 201.5-202° (uncorr.) or 206.5-207° (corr.) with decomposition (Found: C, 82.00; H, 10.64. Calculated for $C_{60}H_{90}O_4$: C, 82.31; H, 10.37%). Mixed melting point with the specimen from ergopinacone prepared by the boiling method 204.5-205.5° (corr.). $[\alpha]_D^{16°} = -202°$ (11.45 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{16°} = -2.31°$). Ultraviolet absorption maximum about 267-275 mμ (indistinct) in 0.055% hexane solution. In the Liebermann-Burchard test the diacetate gives red, violet, blue, and bluish green colours, while in the Rosenheim test pink, violet, dark violet, and finally dark green colours.

Dibenzoate. Prepared from the above ergopinacone (250 mg.). Colourless fine needles (217 mg.), melting at 201.5-202.5° (uncorr.) or 206.5-207.5° (corr.) with decomposition alone or in admixture with the specimen described above (Found: C, 84.43; H, 10.16. Calculated for $C_{70}H_{94}O_4$: C, 84.12; H, 9.48%). $[\alpha]_D^{16°} = -160°$ (14.4 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{16°} = -2.31°$). Ultraviolet absorption maxima in 0.041% hexane solution 280 and 273 mμ (both very sharp). In the Liebermann-Burchard test the dibenzoate gives instantly wine-red, bluish violet, and then bluish green colours, while in the Rosenheim test light pink, light violet, and bluish green colours.

7-Dehydrocholesterol-pinacone and Esters.

Preparation of 7-Dehydrocholesterol-pinacone by the Boiling Method. As described in the previous papers,[4] an alcohol-benzene solution of 7-dehydrocholesterol (383 mg.) and eosin (383 mg.) was boiled to remove air, and exposed to sunlight for several days. Silky long needles (117 mg.) were obtained, and recrystallization from benzene-alcohol gave colourless needles, m.p. 184.5-185.5° (corr.) with decomposition, $[\alpha]_D^{4°} = -175°$ (6.8 mg. in 1 c.c. pyridine solution, $l = 1$ dm., $\alpha_D^{24°} = -1.19°$). No depression of the melting point was observed when the substance was mixed with the specimen prepared by the carbon dioxide method. The melting point, however, was lowered to 180.5° (corr.) after standing in vacuu n half a year.

Diacetate. The above 7-dehydrocholesterol-pinacone (35 mg.) was dissolved in pyridine (7 c.c.) and acetic anhydride (0.7 g.) was added. After standing at room temperature for ten days, the slightly yellowish mixture was poured into ice water, the separating crystals were collected after standing overnight, washed with water, with dilute acetic acid, and again with water, recrystallized twice from benzene-95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (30 mg.), m.p. 185.5-186° (uncorr.) or 190-190.5° (corr.) with decomposition (Found: C, 81.87; H, 10.53. Calculated for $C_{58}H_{90}O_4$: C, 81.81; H, 10.66%). $[\alpha]_D^{26°} = -149°$ (6.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26°} = -1.00°$). Ultraviolet absorption maximum in 0.052% hexane solution 254 mμ (narrow but indistinct), anothor very dim band at about 268 mμ. The substance showed no depression of the melting point when mixed with the specimen of the diacetate described below.

Preparation of 7-Dehydrocholesterol-pinacone Dibenzoate from 7-Dehydrochlesteryl Benzoate by the Boiling Method.[10] 7-Dehydrocholesterol-pinacone dibenzoate (38 mg.) was obtained from 7-dehydrocholesteryl benzoate (158 mg.) in a week's exposure to sunlight. M.p. 183 183.5° (corr.) with decomposition. $[\alpha]_D^{17} = -114°$. No depression of the melting point was observed when the substance was mixed with the specimen of the dibenzoate described below. In the Liebermann-Burchard test the substance gives red, violet, blue, and after standing overnight dark green colours, while in the Rosenheim test pink, dark violet, dark green, and after standing overnight dark brownish violet colours.

Preparation of 7-Dehydrocholesterol-pinacone by the Carbon Dioxide Method. Carbon dioxide was passed through a solution of 7-dehydrocholesterol (383 mg.) and eosin (383 mg.) in 95% alcohol (150 c.c.) for 30 minutes to remove air, and the solution was exposed to sunlight for several days. Small needles which separated out were collected and washed, m.p. 182.5-183° (corr.), yield 180 mg. Recrystallized twice from benzene-alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless needles, m.p. 181-182° (uncorr.) or 184.5-185.5° (corr.) with decomposition, $[\alpha]_D^{24°} = -159°$ (6.8 mg. in 1 c.c. pyridine solution, $l = 1$ dm., $\alpha_D^{24°} = -1.08°$). The melting point was lowered to 182.5° (corr.) on standing in vacuum half a year.

Diacetate. Prepared from the above 7-dehydrocholesterol-pinacone (35 mg.). Colourless fine needles (33 mg.), m.p. 186.5-187° (uncorr.) or 191-191.5° (corr.) with decomposition (Found: C, 82.21, 82.28, 82.04; H, 10.40, 10.68, 10.97. Calculated for $C_{58}H_{90}O_4$: C. 81.81; H, 10.66%). $[\alpha]_D^{26°} = -146°$ (7.25 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26°} = -1.06°$). Ultraviolet absorption maximum in 0.050% hexane solution 254 mμ (narrow but indistinct), another extremely dim band at approximately 268 mμ. In the Rosenheim test the diacetate gives light pink, light violet, then dark green colours.

Dibenzoate. An ice-cooled solution of the above 7-dehydrocholesterol-pinacone (35 mg.) in pyridine (7 c.c.) was mixed with benzoyl chloride (0.8 g.) and the mixture was shaken occasionally for 20 minutes. After standing for a week at room temperature, the mixture was poured into ice water and left to stand for several days. The separating crystals were collected, washed, and recrystallized twice from benzene-alcohol. Colourless needles (31 mg.), m.p. 182.5-183.5° (corr.) with decomposition (Found: C, 83.92; H, 9.45. Calculated for $C_{68}H_{94}O_4$: C, 83.70; H, 9.72%). $[\alpha]_D^{25°} = -113°$ (12.6 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{25°} = -1.43°$).

Preparation of 7-Dehydrocholesterol-pinacone Dibenzoate from 7-Dehydrocholesteryl Benzoate by the Carbon Dioxide Method. A solution of 7-dehydrocholesteryl benzoate (279 mg., m.p. 141.5-143°, clear at 1s7°, corr.) and eosin (279 mg.) in 95% alcohol (400 c.c.) was exposed to sunlight after removing air by passing carbon dioxide. After a week's irradiation the deposit was collected, washed, recrystallized twice from benzene-alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (109 mg.), m.p. 179-180° (uncorr.) or 182.5-183.5° (corr.) with decomposition (Found: C, 83.66; H, 9.51. Calculated for $C_{68}H_{94}O_4$: C, 83.70; H, 9.72%). No depression of the melting point was observed in admixture with other specimens of the dibenzoate described above. $[\alpha]_D^{25°} = -101°$ (12.95 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{25°} = -1.31°$). Ultraviolet absorption maxima in 0.053% hexane solution 280 and 273 mμ (both very sharp). In the Rosenheim test the substance gives light pink, dark violet, dark green, and finally dark brownish violet colours.

Preparation of 7-Dehydrocholestrol-pinacone by the Quick Method. A solution of 7-dehydrocholesterol (227 mg.) and eosin (227 mg.) in 95% alcohol (100 c.c.) was exposed to sunlight after removing air by passing carbon dioxide. After ten hours' irradiation the deposit (75 mg., m.p. 189.5-190.5°, corr.) was collected, purified repeatedly, and dried as usual. Colourless fine needles, m.p. 189-190° (uncorr.) or 192.5-193.5° (corr.) with decomposition. In the Liebermann-Burchard test the substance gives red, violet, and blue colours, while in the Rosenheim test light pink, light red, reddish violet, and finally violet colours. The melting point was lowered with the lapse of time even though the substance was reserved in vacuum: It showed m.p. 187-187.5° (corr.) with decomposition after a month, and m.p. 185.5-186° (corr.) with decomposition after a year. The one year old substance showed a depression of the melting point when mixed with the specimen (m.p. 184.5-185.5°, corr.) prepared by the long exposure method (mixed m.p. 181.5-182.5, corr.).

Summary.

Ergopinacone and 7-dehydrocholesterol-pinacone have been prepared by two different methods, viz., the boiling method and the carbon dioxide method. The products obtained by the two methods as well as diacetates and dibenzoates derived from them have been compared. It has been indicated that the two methods yield the same products.

In conclusion the author wishes to express his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement. He acknowledges also his indebtedness to Dr. K. Yamasaki for his advice and kindness in taking absorption spectra, and to Mr. Yasohachi Yamaguchi and to Ozi Seisi Co. for generous help.

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The Sorption of Gases on Reduced Nickel. II. Sorption of Gaseous Hydrogen Bromide and Hydrogen Chloride and Sorption of Hydrogen Bromide through a Liquid Medium.

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(Received June 23, 1939.)

Reduced nickel reverses the direction of addition of hydrogen bromide to ethenoid compounds, and activates hydrogen bromide in the isomerization of a certain cis compound to its geometrical isomeride. Catechol inhibits the action of reduced nickel in either case. Since such an action of reduced nickel must be closely related to adsorption, the present work has been contemplated. In the previous paper[1] it was shown that at 20° reduced nickel adsorbs hydrogen bromide slowly but abundantly, giving an indication to an activated adsorption. The present paper records the results of experiments on the sorption of hydrogen bromide at 0°C., of hydrogen chloride, and of hydrogen bromide through carbon tetrachloride.

Materials, Apparatus, and Methods. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen bromide was generated by the action of bromine on hot tetralin, passed through cold tetralin, anhydrous calcium bromide, anthracene, and a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon

(1) M. Takebayashi, this Bulletin, **14** (1939), 47.

dioxide and ether, recondensed in a vessel cooled with liquid air, and, after evacuating any uncondensable gases, vaporized, and only the middle fraction was used. Hydrogen chloride was prepared from concentrated hydrochloric acid and concentrated sulphuric acid, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated. Carbon tetrachloride, the purest commercial material, was boiled with alkaline potassium permanganate, washed with water, dried over calcium chloride, and distilled over phosphorus pentoxide. Catechol used was a commercial pure material (Merck).

The apparatus was the same that was used in the previous work. In the experiments on the sorption from carbon tetrachloride a tube as shown in Fig. 1 was used instead of the simple one shown in Fig. 1 of the previous paper.[1]

In every experiment 1.00 g. of reduced nickel was used and treated with hydrogen at 350° as described in the previous paper. Sorption took place under 1 atmospheric pressure of the gases in the dark.

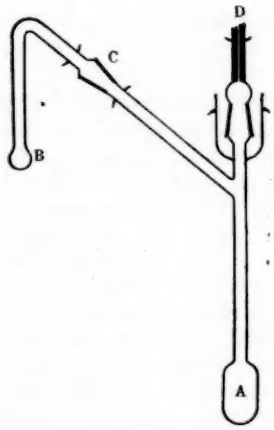

Fig. 1.

Table 1. The Sorption of Hydrogen Bromide on Reduced Nickel (1.00 g.) at 0°C.

Time (min.)	Hydrogen bromide adsorbed (c.c., n.p.t.)
1/2	1.90
1	2.20
2	2.28
3	2.35
5	2.47
10	2 67
20	2.86
30	3.00
50	3.20
70	3.30
100	3.42
130	3.52
160	3.62
190	3.69
1110	4.14
1230	4.12
1545	4.12
2580	4.14

Sorption of Gaseous Hydrogen Bromide. The sorption of hydrogen bromide on freshly reduced nickel was measured at 0°C. The result is given in Table 1. During the first few hours more, but in saturation less, hydrogen bromide is adsorbed at 0°C. than at 20°C. (compare Tables 5 and 6 of the previous paper). This may be another indication to an activated adsorption.

Desorption of hydrogen bromide proceeds slowly in vacuum at 0°C. The reduced nickel which adsorbed 4.14 c.c. of hydrogen bromide at 0°C. to saturation was placed in vacuum for three hours at room temperature; and hydrogen bromide was again introduced at 0°C., when the nickel adsorbed 0.91 c.c. in 1450 minutes and 1.12 c.c. in 1530 minutes. The

partial recovery of the capacity of sorption showed that a part of hydrogen bromide adsorbed on reduced nickel could be desorbed in three hours' evacuation.

Sorption of Gaseous Hydrogen Chloride. The sorption of hydrogen chloride on reduced nickel was observed at 20°C. and 0°C. The results are given in Tables 2, 3, and 4. At any time more hydrogen chloride is adsorbed on reduced nickel at 20°C. than at 0°C. and at either temperature more hydrogen bromide is adsorbed than hydrogen chloride.

The reduced nickel, which adsorbed 3.09 c.c. of hydrogen chloride at 0°C. to saturation and stood in vacuum for three hours, adsorbed at 0°C. 0.68 c.c. of hydrogen chloride in 1440 minutes and 0.78 c.c. in 1560 minutes. Thus it was shown that desorption takes place slowly in vacuum as in the case of hydrogen bromide.

Sorption of Hydrogen Bromide on Reduced Nickel through Carbon Tetrachloride. Since it is in liquid media that reduced nickel has been found to exert the peculiar influence on hydrogen bromide, it seemed desirable to study the sorption in such media. Carbon tetrachloride was chosen as the medium, and the sorption of hydrogen bromide on reduced nickel through this medium and the effect of catechol on the sorption were investigated.

The experimental procedure was as follows: Reduced nickel (1.00 g.), prepared as mentioned above, was taken in sorption tube A (Fig. 1), 1.0 c.c. of carbon tetrachloride or a carbon tetrachloride solution of catechol was poured into side tube B, the volume of the liquid was marked on the tube, and further 0.2 c.c. of pure carbon tetrachloride was added. The side tube was cooled with liquid air, and the whole apparatus was evacuated. Then the metal in the sorption tube was heated at 340-350°C. in the atmosphere of hydrogen to refresh the surface and then in vacuum for an hour to remove hydrogen, and cooled to room temperature. After the treatment of the metal was over, the excess of carbon tetrachloride in tube B was distilled off at room temperature through tube D. In this way any traces of water and air were removed. Then the cock nearest to sorption tube A was closed, tube B was revolved by 180° upward, and the contents of the tube were decanted into tube A, while tube A was cooled in liquid air. Then the sorption tube was warmed to 20°, and the sorption of hydrogen bromide was observed at 20°C.

It was first determined with the sorption apparatus that 1 c.c. of carbon tetrachloride absorbs 5.15 c.c. of hydrogen bromide of 1 atmospheric pressure at 20°C. Then 1 g. of reduced nickel was covered with 1 c.c. of pure carbon tetrachloride, and hydrogen bromide was introduced. The total amount of hydrogen bromide absorbed is given in Table 5. By subtracting the amount absorbed by carbon tetrachloride from the value given Table 5, the amount adsorbed on reduced nickel is found to be 4.27 c.c. The concentration of hydrogen bromide in carbon tetrachloride is about five times as large as in the gas, while reduced nickel adsorbed a little less hydrogen bromide from the carbon tetrachloride solution than from the gas.

Table 2. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.64
1	1.92
3	2.13
8	2.42
13	2.58
23	2.68
38	2.86
53	3.04
98	3.16
128	3.24
1418	3.92
1538	3.94

Table 3. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.68
1	1.90
4	2.18
9	2.38
19	2.54
29	2.67
49	2.77
69	2.84
99	2.93
129	2.98
159	3.02
189	3.06
1470	3.44

Table 4. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 0°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.47
1	1.71
3	1.89
5	2.03
10	2.16
20	2.26
30	2.36
50	2.52
70	2.54
100	2.59
130	2.63
190	2.69
1455	3.09
1590	3.09
1660	3.11
2630	3.09

Table 5. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) at 20°C.

Time (min.)	Hydrogen bromide absorbed (c.c., n.p.t.)
1205	9.26
1440	9.38
1500	9.42

Table 6. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) Containing Catechol (2 mg.) at 20°C.

	Time (min.)	Hydrogen bromide absorbed (c.c., n.p.t.)
I	1365	12.50
	1440	12.58
	1500	12.84
II	1320	12.19
	1440	12.43
	1520	12.52

It was first presumed that the inhibiting action of catechol on reduced nickel was caused by poisoning. Hence, the effect of catechol on the sorption of hydrogen bromide on reduced nickel was studied. Because of the small solubility of catechol in carbon tetrachloride, a solution containing 2 mg. of catechol in 1 c.c. was used. The solubility of hydrogen bromide in carbon tetrachloride was found to be hardly affected by such a small amount of catechol: 1 c.c. of the solution absorbed 5.56 c.c. of hydrogen bromide at 20°C. Then reduced nickel (1.00 g.) was covered with 1 c.c. of the solution and hydrogen bromide was introduced. The total amounts absorbed are shown in Table 6. More hydrogen bromide was absorbed in the presence of catechol, and a simple poisoning was not proved. These results as well as those obtained by O. Simamura in the experiments on the action of hydrogen bromide on catechol and reduced nickel will be interpreted by Y. Urushibara elsewhere.[2]

The author expresses his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to Ozi Seisi Co. for grants.

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The Isomerization of Methyl Allo-cinnamate by Hydrogen Bromide and the Influence of Oxygen.

By **Osamu SIMAMURA.**

(Received July 1, 1939.)

In the previous report[1] an observation concerning the isomerization of dimethyl maleate to the fumarate caused by hydrogen bromide and chloride was described. It was shown that no participation of oxygen in addition to hydrogen bromide is necessary and this type of conversion of cis-trans isomerides was contrasted with that of isostilbene to stilbene[2], which is brought about by the joint action of hydrogen bromide and either oxygen or reduced nickel but not by hydrogen bromide alone nor by hydrogen chloride under any condition at room temperature. In view of the essential function of the carbomethoxyl group in correlation to which were interpreted the experimental results and of hitherto attempted explanations of the nature of the catalysis by hydrogen halides in the

(2) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.
(1) O. Simamura, this Bulletin, **14** (1939), 22.
(2) Y. Urushibara and O. Simamura, *ibid.*, **12** (1937), 507; **13** (1938), 566.

isomerization, a mechanism was tentatively suggested that the hydrogen halide associates with the ethenoid compound by the formation of hydrogen bond through the carbonyl oxygen atom, the accompanying displacement of the shared electrons in the molecule resulting in the more or less diminished rigidity of the double bond.

The scope of the research has since been extended to methyl allo-cinnamate, which has been, in conformity with the expectation from its structure, found to display the behaviour intermediate between dimethyl maleate and isostilbene. Thus, hydrogen bromide converted methyl allo-cinnamate to methyl cinnamate in the dark at room temperature with a slower rate than dimethyl maleate, and the isomerization was accelerated by the presence of oxygen, the action of which was suppressed by catechol added beforehand to the ester. Methyl allo-cinnamate was isomerized by hydrogen chloride very slowly even at an elevated temperature (55°). The formation of methyl cinnamate was also brought about by the addition of a drop of piperidine[3] to 0.1 c.c. of the allo-cinnamate (34% in the course of 24 hours).

These facts add to the possibility of the proposed mechanism of the catalysis by hydrogen halides, in which the presence of a carboalkoxyl group or rather of a carbonyl group conjugated with the double bond is essential. Further, in support of this view it is recorded in the literature that dibenzoyl-ethylene[4] and isobenzaldesoxybenzoin[5] are easily converted by hydrogen chloride into their geometrical isomerides. According to the recent study by Y. Urushibara[6] bromine atoms play a deciding part as chain carriers in the addition of hydrogen bromide to allyl bromide in the presence of oxygen and in the isomerization of isostilbene by the co-operative action of hydrogen bromide and oxygen. As photo-sensitized bromine catalysis in the cis-trans isomerization is widely observed, it seems that the co-operation of hydrogen bromide and oxygen may be rather general irrespective of the nature of the substituents in the isomerizing molecule. In the case of dimethyl maleate the failure of detection of the influence of oxygen may be ascribed to the rapidity of the hydrogen bromide catalysis. With methyl allo-cinnamate the effectiveness of oxygen has been demonstrated.

Materials. The hydrogenation of methyl phenylpropiolate to methyl allo-cinnamate in methanol with palladium deposited on barium sulphate as catalyst yielded a mixture, which could not be easily handled. Then sodium phenylpropiolate was hydrogenated in aqueous solution with the same catalyst to allo-cinnamic acid (Yield 20%), which was converted into the silver salt and finally into the methyl ester by the action of methyl iodide upon the latter suspended in dry ether in the dark at room temperature.[7] The raw product was once distilled in vacuum, b.p. 94° under 1–1.5 mm., n_D^{20} 1.5541. Other materials were obtained and purified as described in the previous report.[1]

(3) Compare G. R. Clemo and S. B. Graham, *J. Chem. Soc.*, **1930**, 213.
(4) C. Paal and H. Schulze, *Ber.*, **35** (1902), 168.
(5) H. Stobbe and K. Niedenzu, *ibid.*, **34** (1901), 3897.
(6) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.
(7) C. Liebermann, *Ber.*, **23** (1890), 2510; **24** (1891), 1107.

Experimental. A clearing point curve of the binary mixture methyl allo-cinnamate–methyl cinnamate was constructed from the following data and subsequent analyses of reaction mixtures were effected by reference to the curve.

Cinnamate (%)	0	10.9	17.7	30.9	39.7	55.4	72.6	85.0	100
Clearing point (°C.)	−3	−7	−9	−4	4.5	17	25.5	31.5	35

Experiments were carried out in the dark at room temperature, procedures being much the same as with dimethyl maleate. In a small glass bulb 0.1 c.c. of methyl allo-cinnamate was taken and after evacuation of the bulb 10 c.c. of hydrogen bromide was introduced, the bulb sealed off and left to stand for about two hours. Then the sealed end of the bulb was crushed in 1% aqueous potassium hydroxide, the oil was taken up in ether, the ether solution washed with water, dried and evaporated. The resulting ester mixture contained 71% of methyl cinnamate. When in addition to hydrogen bromide 3 c.c. of oxygen was admitted, as much as 82% of the allo-cinnamate was isomerized; and 15 mg. of catechol inhibited completely this accelerating action of oxygen, the conversion being 66%, which as about the same magnitude as without oxygen. In a separate experiment catechol was found ineffective in causing the isomerization.

In carbon tetrachloride solution (0.1 c.c. of the ester in 10 c.c.) contained in a tube of a 65 c.c. capacity 23% of the cinnamate was formed by hydrogen bromide (10 c.c.) in four hours. In the same vessel 0.1 c.c. of the allo-cinnamate in 5 c.c. of carbon tetrachloride was isomerized by 5 c.c. of hydrogen bromide in the presence of 20 c.c. of oxygen to the extent of 87% in 22.5 hours and the addition of 25 mg. of catechol reduced the conversion to 62%.

With hydrogen chloride the isomerization took place very slowly and when the reaction temperature was raised to 55°C. it amounted to 14% in the course of 7.5 hours. In carbon tetrachloride under essentially the same conditions as with hydrogen bromide, there was no appreciable formation of the cinnamate with 20 c.c. of hydrogen chloride, whether oxygen was present or not.

The author wishes to express sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragements throughout the work. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to Ozi Seisi Company for grants.

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Studies on the Oiliness of Liquids. VIII. Measurements of the Static Friction Coefficients for Silver Surfaces.

By Toshizo ISEMURA.

(Received May 23, 1939.)

The measurements of the coefficients of static friction of some pure chemical compounds as well as mixtures for glass surfaces were described in the preceding papers.[1] In the complete or film lubrication the surfaces are entirely separated by a thick film of lubricant and the friction depends only upon the nature of the lubricating liquid. It seems that the nature of surface material has no or little effect in this case. In boundary lubrication, however, the surfaces are in contact except for thin film which may be thick by only one molecule layer and the effect of the nature of the solid material can hardly be overlooked. It is important to measure the static friction coefficients with the surfaces of different materials. In the present paper, the measurement of the static friction coefficient for silver surfaces is described. The friction surfaces used consisted of a silver plate and a silver slider with convex spherical surface.

The experiments were pursued by the balance method. The cleanliness of the surfaces is of the utmost importance for the measurements of the static friction coefficients. The surfaces are cleaned in the following manner before each observation. The silver plate and the slider are polished with *rouge*-paper on a grinder, then with cloth and at last with leather or flannel to remove any scratches on the surfaces as completely as possible. After polishing, the surfaces are cleaned by electrolysis. A mixture of equal volumes of 1% aqueous solution of caustic soda and alcohol is taken as the electrolytic solution. The electrolytic cell consists of a platinum anode and a silver cathode. Electrolysis is conducted at 6 volts and less than 0.2 amp., for 30~60 minutes. After this treatment, the silver plate and the slider are rinsed with distilled water and then with drains of distilling alcohol and dried in a desiccator by passing a current of dry air. The silver surfaces cleaned by such a procedure are readily wetted with water and the friction coefficient of the surfaces with no lubricant is very high and fairly concordant in every experiment. It is a somewhat difficult matter to determine the cleanliness of the surface of silver. The friction coefficient itself is a very good criterion. The clean surfaces stick strongly and show a high friction coefficient. At first, the static friction coefficient of silver with no lubricant was determined. The results are shown in Table 1.

For the measurements of static friction coefficients of organic liquids, the friction coefficient of silver with no lubricant is measured prior to each experiment. If the value of the friction coefficient of silver surfaces

(1) Sameshima, Kidokoro and Akamatsu, this Bulletins, **11** (1936), 659; Akamatu and Sameshima, *ibid.*, **11** (1936), 791; Sameshima and Tsubuku *ibid.*, **12** (1937), 127; Akamatu, *ibid.*, **13** (1938), 127; Isemura, *ibid.*, **14** (1939), 270.

is larger than 0.9, it was assumed that the surfaces are clean. The further measurements were conducted with these clean surfaces.

Table 1.

	W	F	μ
No lubricant	9.10	9.36	1.03
	10.30	10.78	1.05
	14.10	14.02	1.00
	14.90	17.02	1.14
	19.90	22.55	1.13
	20.20	19.88	0.98
	20.25	19.66	0.97
	20.30	21.92	1.08
	30.25	29.95	0.99
	30.25	31.83	1.05
			1.04

As to the cleaning of the steel surfaces, Hardy[2] wrote as follows: "Steel plates and sliders were cleaned by washing with soap and water, rubbing vigorously with the finger tips in a stream of tap water until water wetted the entire surface, rinsing with perfectly dry alcohol and allowing to drain in air." However, when the silver surfaces were washed with soap and rinsed with water, the surfaces entirely repelled water. The surface could not be wetted with water by rubbing the surface with finger tips in the stream of tap water. Probably, the soap molecules are strongly adsorbed by the surface and take orientation on it, the polar group being attached to the surface. These surfaces show very low friction coefficients as shown in Table 2. The greater part of soap is removed rinsing the surfaces with alcohol. It is difficult however, to obtain sufficiently clean surface.

Table 2.

	W	F	μ
Both plate and slider are washed with soap.	30.25	6.80	0.22
	60.25	10.23	0.17
	63.65	11.40	0.17
			0.19
Only plate is washed with soap, clean slider.	30.25	5.13	0.17
	38.65	7.18	0.19
			0.18
Only slider is washed with soap, clean plate.	30.30	10.34	0.34

In the present experiment, the friction coefficients have been measured of water, alcohols, acids, hydrocarbons and esters. The purest samples available were used. Alcohols, acids and esters were distilled prior to each expriment, after sufficient drying with the appropriate drying agents. As already reported in the former paper,[3] the aliphatic hydrocarbons such as hexane, contain some unsaturated hydrocarbon as impurities.

(2) Hardy and Doublrday, *Proc. Roy. Soc.* (London), A, **100** (1922), 550.
(3) Akamatu, this Bulletin, **13** (1938), 127.

These impurities cannot be removed merely by distillation. The samples containing these impurities give somewhat lower friction coefficients. So the hydrocarbons used in the present experiment were purified by shaking with fuming sulphuric acid for several days, dried over sodium metal and distilled.

The results obtained are shown in Table 3. The values of friction coefficient against the number of carbon atoms are plotted in Fig. 1 and Fig. 2.

Table 3.

	W	F	μ		W	F	μ
Water	18.65	16.50	0.88	Ethyl alcohol	18.65	16.05	0.86
	20.25	16.85	0.83		20.25	17.73	0.88
	20.30	18.88	0.93		23.65	20.10	0.85
	30.25	28.40	0.94		28.65	26.43	0.92
	41.90	40.10	0.96		30.25	26.20	0.87
			0.91				0.88
Hexane	15.20	15.20	1.00	*n*-Propyl alcohol	28.64	22.80	0.80
	18.70	16.92	0.90		30.25	25.68	0.85
	20.20	18.50	0.92		30.25	23.98	0.79
	20.30	19.20	0.95		30.30	27.70	0.91
	23.60	24.25	1.03				0.84
			0.96				
Heptane	14.10	13.00	0.92	*n*-Butyl alcohol	18.65	15.11	0.81
	14.80	13.75	0.93		19.10	14.90	0.78
	17.50	16.75	0.96		20.25	14.30	0.71
	18.20	17.13	0.94		20.25	15.68	0.77
	19.10	18.05	0.95		30.25	22.52	0.74
	22.55	20.55	0.91		30.25	22.50	0.74
			0.94				0.76
Octane	14.10	14.28	1.01	*n*-Amyl alcohol	20.25	13.23	0.65
	14.90	13.72	0.92		23.65	15.30	0.65
	17.30	17.38	1.00		29.90	20.20	0.68
	17.50	16.90	0.97		30.25	18.35	0.61
	19.90	18.50	0.93				0.65
			0.97				
Benzene	18.65	17.76	0.95	*n*-Hexyl alcohol	14.10	9.42	0.67
	20.25	19.13	0.95		14.90	10.00	0.67
	22.70	23.60	1.04		17.50	10.82	0.62
	23.20	22.60	0.95		19.10	12.90	0.68
	23.65	24.10	1.02		22.50	14.48	0.64
	25.65	24.10	0.94				0.66
	28.20	26.70	0.95				
			0.97	*n*-Heptyl alcohol	20.25	11.55	0.57
					28.65	15.92	0.56
Methyl alcohol	14.10	11.82	0.84		30.30	16.85	0.56
	14.90	13.38	0.90		38.70	21.00	0.54
	18.30	16.50	0.90				0.56
	18.30	17.05	0.93				
	19.90	17.50	0.88	*n*-Octyl alcohol	19.10	10.69	0.56
	23.30	21.73	0.93		22.50	13.30	0.59
			0.90		23.70	11.65	0.49
					30.30	15.52	0.51
					30.30	14.73	0.49
							0.53

Table 3.—(*Concluded*)

	W	F	μ
Acetic acid	14.10	12.98	0.92
	18.65	17.78	0.95
	20.30	17.68	0.87
	28.65	25.70	0.90
	30.30	27.66	0.91
			0.91
Propionic acid	20.25	16.40	0.81
	28.65	23.35	0.82
	30.25	25.78	0.85
	38.65	33.42	0.86
			0.84
Butyric acid	20.25	15.10	0.75
	20.30	13.40	0.66
	30.25	21.12	0.70
	30.30	22.10	0.73
			0.71
Valeric acid	19.90	11.85	0.60
	23.30	13.80	0.59
	28.70	17.90	0.62
	29.90	17.20	0.58
	30.25	17.50	0.58
			0.59
n-Caproic acid	20.25	11.20	0.55
	23.65	12.40	0.52
	28.65	14.81	0.52
	30.25	16.44	0.54
	30.25	17.12	0.57
	38.65	21.20	0.55
			0.54
n-Heptylic acid	20.25	8.74	0.43
	28.65	13.02	0.45
	30.25	12.63	0.42
	38.65	18.10	0.47
	41.85	19.70	0.47
	60.25	25.68	0.43
			0.45
n-Caprylic acid	41.85	13.82	0.33
	60.25	18.60	0.31
	68.65	20.40	0.30
			0.31
n-Nonylic acid	41.85	11.44	0.27
	46.90	12.75	0.27
	51.85	14.45	0.28
	55.30	14.92	0.27
	60.25	16.75	0.28
	68.70	18.14	0.26
			0.27
Oleic acid	30.25	7.02	0.23
	38.65	9.54	0.25
	41.95	9.65	0.23
	46.50	12.30	0.26
	51.95	12.70	0.24
			0.24
Ethyl acetate	10.25	8.84	0.86
	20.25	16.30	0.81
	20.30	16.10	0.79
	30.30	24.80	0.82
			0.82
n-Propyl acetate	20.25	15.55	0.77
	23.65	17.15	0.73
	28.65	20.28	0.71
	30.30	21.88	0.72
	38.65	27.20	0.70
	38.65	28.12	0.73
			0.73
n-Butyl acetate	20.25	14.00	0.69
	28.65	19.70	0.69
	28.70	19.98	0.70
	30.25	20.25	0.67
	38.65	24.44	0.63
			0.68
n-Amyl acetate	20.25	13.50	0.67
	20.25	14.90	0.74
	30.25	18.69	0.62
			0.68
n-Octyl acetate	20.30	12.90	0.64
	20.30	13.13	0.65
	28.65	17.48	0.61
	30.30	19.20	0.63
	38.65	22.40	0.58
			0.62
Ethyl propionate	14.10	11.62	0.82
	17.50	14.22	0.81
	18.30	15.18	0.83
	23.30	19.53	0.84
			0.83
Ethyl butylate	20.25	15.46	0.76
	20.30	15.88	0.78
	30.25	22.90	0.77
			0.77

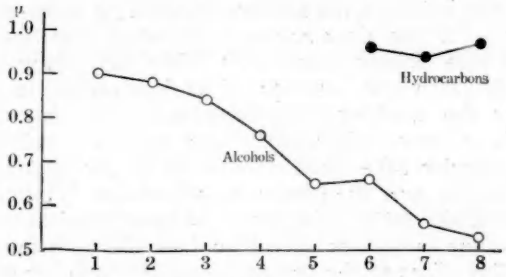

Fig. 1.

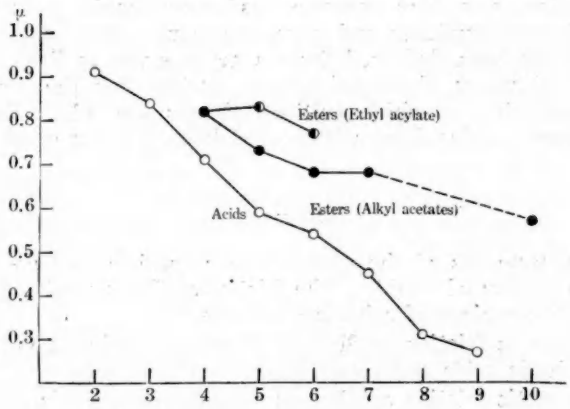

Fig. 2.

Hydrocarbon such as hexane, heptane, octane and benzene give very high friction coefficients. The μ-values are almost the same with the value of clean surface. The lubricating activity is practically nil with these substances. The compounds of low molecular weight such as acetic acid, methyl alcohol, ethyl acetate and water are always poor lubricants irrespective to their species. In the cases of acids, alcohols and esters, the coefficients of friction are diminished as the length of the chains is increased. With lower homologues, there is no appreciable difference between the lubricating activities of acids, alcohols and esters. But with the compounds of fairly long chains acid is most efficient lubricant and alcohol comes next. Ester is most inefficient among the three. The results with alcohols and esters are almost comparable with the results on glass surfaces.[4][5] Regarding to the μ-values of acids, there is a

(4) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127.
(5) T. Isemura, *ibid.* **14** (1939), 270.

striking difference between the results obtained on glass surfaces and on silver surfaces. On the glass surfaces, the static friction coefficients of aliphatic acids are nearly constant,[4] while on silver surfaces, they diminish rapidly with the number of carbon atoms in the molecular formulae. For the washing with soap we know that the long chain molecules such as soap adhere to silver surface much better than to glass. The molecules take good orientation on the silver surface. The longer the molecules are, the better the orientation is taken. From these facts the long chain fatty acids serve as good lubricants. The regular arrangement of the molecules on the surface plays an important rôle on the oiliness. The effect of the arrangement of the molecules was already reported in the previous paper.[6] This is probably the reason why the long chain fatty acids shows the low friction coefficients.

In conlusion the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokai (Japan Society for the Promotion of Scientific Research), to which author's thanks are due. The author's acknowledgment is also due to Hattori Hokokwai for a grant.

Summary

(1) Measurements of the static friction coefficients have been made to study the oiliness of liquids. The friction surfaces consisted of a silver plate and a silver piece of spherical surface.

(2) The static friction coefficients of water, hydrocarbons, aliphatic alcohols, aliphatic acids and esters have been measured.

(3) The static friction coefficients of these compounds excepting the acids are all comparable with the results obtained for the glass surfaces. The friction coefficients of acids diminish rapidly with the number of carbon atoms in the chain of the molecule for the silver surfaces, while they are nearly constant irrespective to the number of carbon atoms for glass surfaces.

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(6) Akamatu and Sameshima, this Bulletin, **11** (1936), 791.

The Occurrence of Germanium in the Hot Springs of Senami.

By Kazuo KURODA.

(Received June 29, 1939.)

Germanium occurs in quite appreciable amounts in some mineral waters.[1] J. Bardet reported germanium to be present in the mineral waters of Vichy to the extent of one part in 40,000,000 parts of water. In this country, it was also found spectroscopically by Prof. K. Kimura in a large number of mineral waters.[2] In the present work the author attempted a spectroscopic estimation of the element in the hot springs of Senami, Niigata Prefecture.

Arc Spectrographic Estimation of Germanium. J. Papish and his collaborators[3] described a method of the arc spectrographic estimation of germanium, in which the germanium solution was placed on the lower electrode. In the present paper the author describes a method in which germanium is added to sodium chloride in various concentrations. 0.1441 g. of pure germanium dioxide was dissolved in water and the volume was made up to 100 c.c. Each c.c. of this solution contains 1 mg. of germanium. From this stock solution, solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg. of germanium per c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actcually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg of germanium respectively. The Hilger spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 1. In this table, S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

Table 1. Spectral Lines at Different Concentrations.

λ (Å)	1 mg	0.1 mg	0.01 mg	0.001 mg	0.0001 mg	0.00001 mg
2198.7	F					
2314.2	W					
2327.9	W					
2338.6	F					
2379.1	W					
2394.1	F					
2397.9	F	F				
2417.4	S	W	W	F		
2498.0	W					

(1) J. Bardet, *Compt. rend.*, **157** (1913), 224; **158** (1914), 1278; A. P. Forjaz, *Compt. rend.*, **186** (1928), 1366; **189** (1929), 703.

(2) Not yet published.

(3) J. Papish, F. M. Brewer and D. A. Holt, *J. Am. Chem. Soc.*, **49** (1927), 3028.

Table 1.—(*Concluded*)

λ (Å)	1 mg	0.1 mg	0.01 mg	0.001 mg	0.0001 mg	0.00001 mg
2533.2	S	W				
2556.3	W					
2589.2	W	F				
2592.6	S	W	W	F		
2644.2	W	F				
2651.1	S	S	W	W	W	F
2651.6	S	S	W	W	F	
2691.3	S	S	W	W	F	
2709.6	S	S	W	W	F	
2740.4	S	F				
2754.6	S	S	W	W	F	
2793.9	W					
2829.1	W					
3039.1	S	S	W	W		
3067.1	W					
3124.8	W	W				
3269.5	S	W	F			

Germanium Content of the Hot Springs of Senami.[4] 500 c.c. of water sample was evaporated to complete dryness. Finely powdered residue in ten milligram portions was subjected to arc excitation. The following germanium lines were always found:—

λ (Å)	Intensity
2651.1	weak
2651.6	faint
2691.3	faint
2709.6	faint
2754.6	faint

This would seem to indicate that 0.0001 mg. of germanium was present in the zone of excitation. Expressed in percentages, the germanium content in the total residue is estimated to be 0.001. Expressed in terms of parts per million of the mineral water, it is supposed to be 0.03.

Summary.

A method for the arc spectrographic detection and estimation of germanium was described.

The germanium content of the hot springs of Senami was estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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(4) According to R. Ishizu, the spring is classified as common salt spring.

The Occurrence of Beryllium in the Hot Springs of Matunoyama.

By Kazuo KURODA.

(Received June 29, 1939.)

Beryllium occurs in a great many minerals, but rarely in mineral waters.[1] Prof. K. Kimura found the occurrence of beryllium in the hot springs of Matunoyama, Niigata Prefecture, and in the present work the author attempted a spectroscopic estimation of the element.

Arc Spectrographic Estimation of Beryllium. Pure beryllium sulphate was dissolved in water. The beryllium content of this solution was determined gravimetrically and water was added to bring the concentration to 0.1 per cent. From this stock solution, solutions containing 0.01, 0.001, 0.0001, 0.00001, 0.000005, 0.0000025 and 0.000001 g. of beryllium per 100 c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001, 0.0001, 0.00005, 0.000025 and 0.00001 mg. of beryllium respectively. The Hilger quartz spectrograph of E2 type was used. The spectral lines observed at different concentrations are given in Table 1. In this table,

Table 1. Spectral Lines at Different Concentrations.

λ (Å)	1 mg	0.1 mg	0.01 mg	0.001 mg	0.0001 mg	0.00005 mg	0.000025 mg	0.00001 mg
2348.6	S	S	S	S	W	W	F	
2350.8	S	W	F					
2494.7	S	S	S	W	F			
2650.8	S	S	S	W	F			
2738.1	F							
2898.2	W							
2986.1	F							
3019.3	F							
3110.8	W	F						
3130.4	S	S	W	W	W	W	F	F
3131.1	S	S	W	W				
3187.3	F							
3321.1	S	S	W	W	F			
3321.4	S	S	W	W	F			

(1) A. Béchamp, *Compt. rend.*, **62** (1866), 1088; Pomier, *J. pharm. chim.* [2], **14** (1928), 199; M. Mazade, *Compt. rend.*, **32** (1851), 685.

S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

Beryllium Content of the Hot Springs of Matunoyama. 1600 c.c. of water sample was evaporated to complete dryness. The residue was treated with hydrochloric acid and filtered. The residue which mainly consisted of silica showed no beryllium when examined spectroscopically. The chloride solution was evaporated to dryness, heated to 130° in the air bath, and weighed. Finely powdered residue in ten milligram portions was subjected to arc excitation. The beryllium lines 2348.6 (weak) and 3130.4 (faint) were always found. This would seem to indicate that a quantity higher than 0.000025 mg and lower than 0.00005 mg of beryllium was present in the zone of excitation. Expressed in percentages, the beryllium content in the total residue is estimated to be between 0.00025 and 0.0005. Expressed in terms of parts per million of the mineral water it is supposed to be between 0.04 and 0.08.

Summary

A method for the arc spectrographic detection and estimation of beryllium was described.

The beryllium content of the hot springs of Matunoyama was estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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